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# Molecular Weight Distribution Broadening of Polypropylene by Periodic Switching of Hydrogen and Catalyst Additions

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**ABSTRACT:** This study presents a feasibility study of the broadening of the polypropylene molecular weight distribution produced using a multisite Ziegler-Natta catalyst in a continuous liquid-pool polymerization reactor. The broadening is achieved by operating the reactor under periodic forcing of both hydrogen and catalyst feed flows. Model-based dynamic optimization is used to determine the cycle period and peak width for these inputs. Through simulation it is shown that limited widening (~ 30%) of the molecular weight distribution

can be achieved in case of a limited removal of hydrogen from the reactor. The results also show that the forced removal of hydrogen from the reactor could potentially double the polydispersity index of the produced polymer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2446–2457, 2008

**Key words:** molecular weight distribution broadening; liquid-pool polymerization; periodic operation; control vector parameterization

## INTRODUCTION

Control of the molecular weight distribution (MWD) of polymers is important because it influences the final mechanical and processing properties of the polymer. Industrially, there is a strong demand to produce polymers having both short and long chains. The presence of short chains is required to give good processability to the polymer; whereas the high molecular weight fraction provides good mechanical properties. This makes it desirable to produce polymers with a broad MWD.

### Controlling MWD

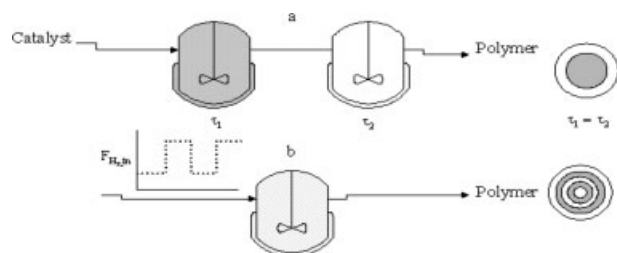
Theoretically, any desired form of the MWD can be produced by appropriate fractionation of very broad molecular weight polymer or blending narrowly distributed polymers. Fractionation is not employed because of different reasons; the main reason is the relatively high cost of this operation.<sup>1</sup> Blending is not widely used, because most of the catalysts produce widely-distributed polymers. Moreover, producing polymers, which are mixed on microscale

level, requires a melting process, which is not economical. To avoid difficult post-synthesis operations, the aim is to produce polymers with the appropriate MWD directly in the polymerization reactor(s). All the alternative techniques rely on a simple experimental principle: mixing of different polymer materials at the molecular level. This can be achieved using one of the following methods:

1. Using a mixture of different metallocenes<sup>2–7</sup> or a hybrid catalyst of Ziegler-Natta and metallocene catalysts in a one stage process.<sup>8–10</sup> This approach has an advantage that one reactor is required. However, for each polymer grade a sophisticated catalyst has to be developed to adjust the amount, and the MWD of both fractions formed in the polymerization reaction. Moreover, the mixture of different catalysts may lead to non-reproducible catalyst behavior due to the high variability of the polymerization rate of each catalyst. In addition, such implementation requires a thorough understanding of polymerization mechanisms using these catalysts, which is still in the research phase and it may take a long time before it can be (if it is developed successfully) widely implemented in industry.
2. Polymerization in reactor cascades, where each reactor is operated at different polymerization conditions (usually hydrogen concentration). This technology is commonly used with

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**Figure 1** Homogeneity of polymers using different production technologies.

Ziegler-Natta catalysts. It has the advantage that only one optimized catalyst is required for the production of various grades. The problem with this approach is that the polymer has low homogeneity of the two (or more) polymer grades and the final polymer particle has a core-shell-like structure [Fig. 1(a)]. Additionally, this method is subject to high operational costs.<sup>11</sup>

3. Variation of polymerization conditions, especially the concentration of chain transfer agents, in a single reactor. This approach has the advantage of requiring a single reactor, which simplifies process design and reduces the operational costs. Furthermore, the periodic operation of continuous chemical reactors can improve the performance of the reacting system and allow better design and control of the MWD in a single reactor.<sup>1,12</sup> An example of a process with variation of process conditions is the multizone reactor developed recently by Basell.<sup>13,14</sup> The product of a single reactor compared with multiple reactors has improved polymer homogeneity and assures that the ratio of both polymer products in each particle is equal to the overall ratio of these products [Fig. 1(b)]. However, the dynamic operation of the polymerization reactor is difficult and it is subject to appreciable production of off-specification products.<sup>11</sup>

The broadening of the MWD using the second and third approaches implies the production of off-specification products, consequently, the transition period must be as short as possible. Thus, most of the work done in this field focuses on finding the optimal profiles for the manipulated variables. In this work, the oscillatory operation of the polymerization reactor, i.e., the third option mentioned above, is investigated with the objective of producing polypropylene with a broad MWD.

### Periodic operation of polymerization processes

Most chemical processes are nonlinear in nature. The nonlinear behavior offers the opportunity to improve the time-averaged performance, such as conversion

and parametric sensitivity of chemical processes, by unsteady state periodic or cyclic operation. In the last 3 decades, the implementation of periodic operation as a mean of improving process performance has been the subject of many experimental and computational investigations.<sup>15–18</sup>

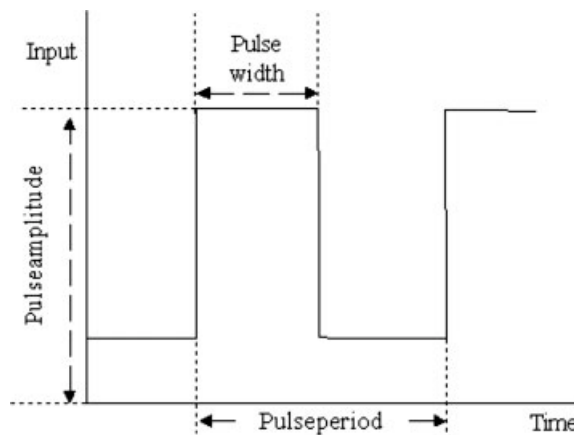
For cyclic operation, two types of forcing functions have been employed in the literature, namely sinusoidal inputs and rectangular pulses.<sup>19</sup> The latter approach, which is also known as the bang-bang type, has been shown to be the optimal forcing function.<sup>20</sup> This is due to the fact that the rectangular pulse produces the most abrupt disturbance as shown in Figure 2. In addition, this type of control is quite simple to implement. Thus, it will be considered in this investigation.

Forced oscillations in continuous free-radical polymerizations have been studied in several occasions.<sup>21–25</sup> These investigations involved in all cases continuous stirred tank reactors (CSTRs) and sinusoidal or square waves. Most publications considered the periodic operation of the monomer and/or the initiator. These studies considered this type of control from both a theoretical and an application point of view. However, none of them have considered the optimal control problem.

The available literature regarding the periodic control of Ziegler-Natta polymerization reactors is limited. Claybaugh and Giffinand<sup>26</sup> experimentally investigated the influence of the periodic feeding of hydrogen on propylene polymerization by a  $\text{TiCl}_3$  catalyst. They assumed that the number average molecular weight being produced ( $M_n$ ) is a simple function of the hydrogen concentration ( $C_{\text{H}_2}$ ):

$$M_n = \frac{k}{C_{\text{H}_2}} \text{ or } M_n = \frac{k}{\sqrt{C_{\text{H}_2}}} \quad (1)$$

where  $k$  is a constant. The required hydrogen flow rate profile can be calculated according to the desired



**Figure 2** Bang-bang cyclic strategy.

MWD. However, this approach<sup>1</sup> has many limitations amongst others, the assumption that a simple relationship exists between the number average molecular weight and the hydrogen concentration.

Lee and Bailey<sup>27</sup> investigated theoretically the combined effect of imperfect mixing conditions with a bang-bang cyclic operation on Ziegler-Natta catalyzed olefin polymerization in a CSTR reactor. For this investigation, the authors used the experimental data given by Claybaugh et al.<sup>26</sup> In investigating the bang-bang forced oscillations in the hydrogen concentration, the authors concluded that such oscillations and imperfect mixing can significantly enlarge the MWD compared with the MWD attained at steady-state conditions. The authors examined the effect of very fast and very slow cycling on reactor behavior. In the former case, it was found that the reactor filters the oscillations fast, such that system variables are approximately time-invariant; whereas, in the latter case, the reactor remains close to the steady state conditions at every instant. Finally, it is worth mentioning that polydispersity values for perfectly mixed CSTR were low,  $\sim 2.0$ , which is unexpected for Ziegler-Natta catalysts.

In his patent, Schiffrino<sup>12</sup> discussed the broadening of the MWD of polyolefins produced in a short residence time tubular reactor using a Ziegler-Natta catalyst. The reactor is operated in a semicontinuous mode with single or multiple catalyst feeds and staged monomer feeds to minimize off-specification product, optimize and control molecular weight and MWD of the produced polymer. However, this research was performed in a laboratory scale reactor with a limited volume ( $\sim 50 \text{ cm}^3$ ) and short residence time ( $\sim 500 \text{ s}$ ), which makes its industrial application questionable.

In a simulation study, Nele and Pinto<sup>28</sup> described the continuous production of polypropylene with broadened MWD through the periodic variation of polymerization temperature, hydrogen and monomer concentrations. The authors developed an objective function for finding the optimal trajectory of the selected manipulated variable. In this objective function, they considered the number average molecular weight and the polydispersity index (PDI). It is worth mentioning that the authors intended to increase the PDI from 2 to 5. The results showed that by manipulating hydrogen concentration and reaction temperature, the desired targets were achieved, however, with many oscillations. Meanwhile, manipulating monomer flow rate, alone, was not sufficient to reach the required targets. Two important remarks should be made: (i) the authors used a single-site metallocene catalyst and (ii) the changes in the hydrogen pressure and temperature are high, 6.0 bars and  $50^\circ\text{K}$ , respectively.

This review shows that there is no study, which uses multisite Ziegler-Natta catalysts in a single reac-

tor and explores the effect of changing the manipulated variables periodically on polymer MWD. Thus, the focus in this investigation is on studying the broadening of the MWD of polypropylene. This will be performed by varying the inlet flows of hydrogen and catalyst periodically. The characteristics of these periodic inputs will be determined using model-based dynamic optimization techniques. The broadening will be monitored by the PDI. Interested readers can find details about the process and models in Al-haj Ali.<sup>29</sup>

## PROCESS MODELING

### Process description

The process model describes a pilot-plant propylene homopolymerization process, which consists of a hollow shaft reactor<sup>30</sup> followed by an expansion vessel. The process is used to make various grades of polypropylene. These grades are characterized by the weight average molecular weight ( $M_{wc}$ ) and a complete MWD of the polymer product. Olefin polymerization kinetics with Ziegler-Natta catalysts are fairly complex. The subject has been discussed in a previous work.<sup>31</sup>

The feed to the reactor consists of the monomer, the transfer agent (hydrogen), and the catalyst. The reactor temperature is kept constant by controlling the jacket temperature using a PI controller. The reactor is equipped with a double-valve chamber and a backpressure valve to control the reactor pressure by manipulating the reactor outlet flow rate. Therefore, the variation in reactor pressure will not be described by the model but assumed constant.

The feed flows and reactor pressure are measured along with the reactor and jacket temperatures.

### Model development

The process model consists of dynamic material balances including rate expressions, an energy balance equation, and dynamic balance for the MWD in addition to the algebraic equations for the physical properties. To achieve the defined objectives, it is not necessary, under the proposed operating conditions, to consider the variation in temperature and concentration inside the polymer particles. It may be assumed that concentrations and temperature spatial variations in the reactor are negligible.<sup>30</sup> Thus, the proposed model consists of a set of ordinary differential equations combined with algebraic equations. Model equations are listed in Appendix A.

### Optimal control problem

In this study, it is intended to produce a MWD with a maximum PDI. Simulations<sup>32</sup> show that such a



polydispersity fluctuates between the band limits; thus, an average value ( $PDI_{avg}$ ) is introduced. Consequently, the objective function is defined as:

$$J = \int_{t_0}^{t_f} \left[ w_1 \left( \frac{PDI_{reference}}{PDI_{reference} - PDI_{avg}} \right)^2 + w_2 \left( \frac{C(t) - C_{sp}}{C_{sp}} \right)^2 \right] dt \quad (2)$$

where  $PDI_{reference}$  is polypropylene PDI before broadening is started, it has a value of 7.0 and  $C$  is polymerization conversion. At optimum,  $C = C_{sp}$  and  $PDI_{avg}$  will be maximum. To accelerate the broadening procedure, 10% band limits, which are comparable with the gel permeation chromatography measurement error, are defined.

The economical aspect of the broadening problem is represented by the conversion term. Note that, in contrast to the grade transition problem, the conversion is controlled along the entire time horizon. Depending on the weights  $w_1$  and  $w_2$ , the significance of conversion will vary.

Both hydrogen and catalyst flow rates are chosen as the manipulated variables. As stated earlier, square-wave perturbations in these variables are considered. The rectangular pulse is described by three parameters (Fig. 2): cycle period, amplitude, and cycle width. The optimization problem studied in this work focuses on finding the best characteristics for the cycles of hydrogen and catalyst. Four operating parameters (two for hydrogen and two for the catalyst), which are cycle period and width have been selected as the optimization variables. The upper bound on the inlet hydrogen flowrate (cycle amplitude) has a pre-assigned value that is changed for different optimization cases whereas the upper bound for the catalyst feed rate is fixed at 0.01 g/h. Note that the steady state hydrogen flow rate, i.e.,  $t < 10$  h, was chosen so that the time average hydrogen flow rate is constant over the entire simulation.

The optimal control problem is solved using control vector parameterization technique.<sup>33,34</sup> By using this method, the continuous optimal control problem is transformed into a finite dimensional optimization problem such that the problem can be solved using existing nonlinear programming packages. In this article, the MATLAB SQP function is used as the optimization algorithm and a MATLAB S-function serves as a dynamic process simulator.

## RESULTS AND DISCUSSION

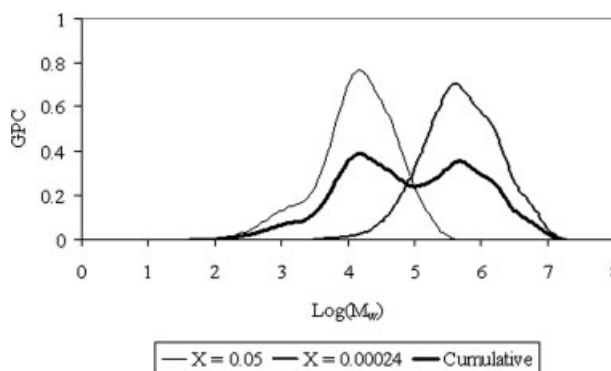
The degree of polymer broadening that can be achieved is dependent on several conditions. Two cases will be considered:

1. Finding the maximum achievable PDI that can be produced by operating the polymerization reactor under rectangular pulse perturbations in either hydrogen feed rate or both hydrogen and catalyst feed rates. In this case, hydrogen can only be removed by washing out.
2. Maximizing the PDI using the approach mentioned above; but assuming that there is an efficient technique for hydrogen removal.

### Finding maximum achievable broadening

Before we proceed with discussing the results, it is worth considering the broadening obtained in case equal amounts of polymers are produced in a batch reactor by introducing a step change in hydrogen concentration from  $X = 0.00024$  to 0.05, where  $X$  is the molar ratio of hydrogen to monomer. The hydrogen ratio inside the continuous reactor oscillates between these two values as will be shown later. Figure 3 shows that the polymer produced has a bimodal distribution. Therefore, the continuous production of polypropylene with a similar distribution should be possible provided that hydrogen can be removed fast enough from the reactor. Thus, under isothermal conditions, this distribution is the maximum obtainable for the used catalyst within the range of hydrogen concentrations considered.

The broadening maximization is done with equal weights on polydispersity and conversion. In this case, the hard constraint on the hydrogen feed rate is relaxed. The initial guesses for the optimization routine were obtained by testing the reactor performance using oscillatory hydrogen feed rates with different characteristics.<sup>32</sup> On the basis of these simulations, it was concluded that the period of oscillation should be long enough to allow marked changes in the reaction medium. On the other hand, the oscillation period should be short enough to permit



**Figure 3** Cumulative distribution of polypropylene produced in a batch reactor at constant temperature,  $T = 70^{\circ}\text{C}$ .

TABLE I  
Pulse Characteristics and Polymer Properties for Maximization of PDI

Forcing function	Hydrogen pulse			Catalyst pulse			$M_{nc}$ (kg/mol)	PDI	$\bar{\tau}$ (h)	$\frac{\bar{\tau}}{\bar{P}}$
	$P$ (h)	$W$ (h)	$A$ (g/h)	$B$ (g/h)	$W$ (h)	$A$ (g/h)				
Steady state	–	–	–	0.005	–	–	8.02	7.2	0.84	–
Periodic										
Constant conversion	2.90	0.96	2.77	0.005	–	–	8.48	9.3	0.87	0.30
Variable conversion	2.77	0.85	2.87	0.0036	0.80	$-3.5 \times 10^{-3}$	9.99	9.97	0.82	0.30
Periodic										
Forced hydrogen removal										
$R_{removal} = 0.5$ (Fig. 6)	2.44	0.86	1.47	0.0065	1.2	$0.9 \times 10^{-3}$	10	11	0.91	0.37
$R_{removal} = 0.5$ (Fig. 7)	2.94	0.88	0.73	0.007	0.80	$-5.1 \times 10^{-3}$	25	14	0.88	0.30
$R_{removal} = 50$ (Fig. 8)	2.45	1.0	1.58	0.007	0.80	0.0	40	12.5	0.90	0.37

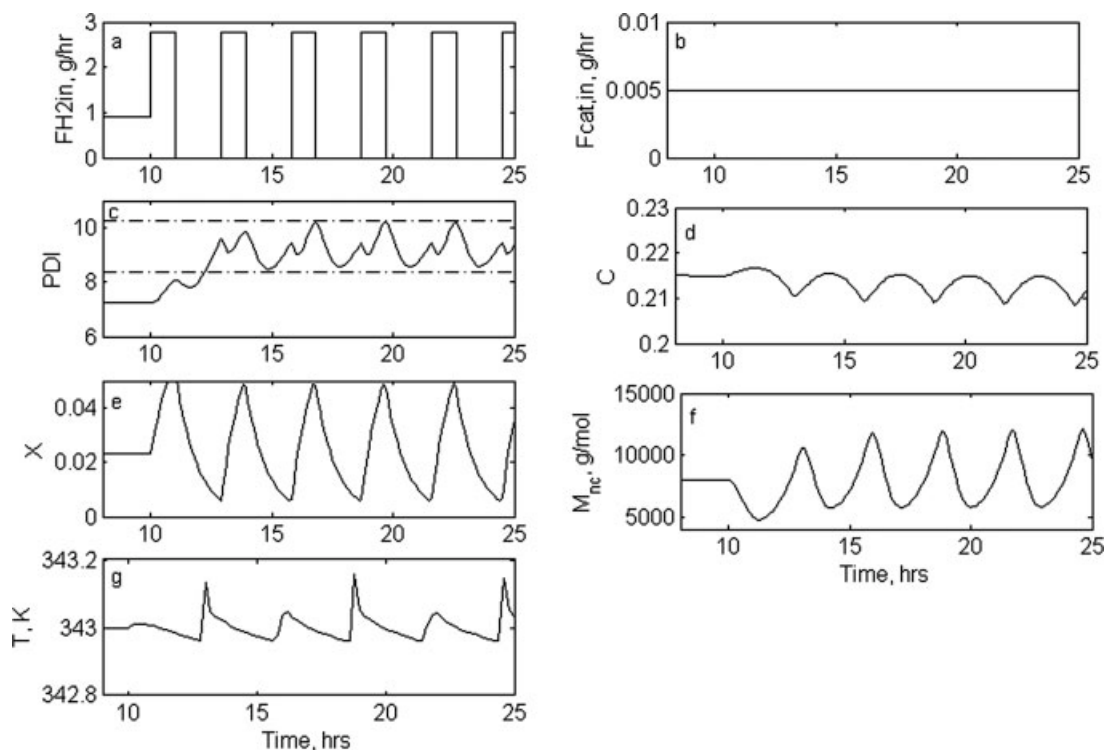
$P$ , cycle period;  $W$ , pulse width;  $A$ , pulse magnitude;  $B$ , steady state catalyst feed rate.

adequate blending of the reactor contents, thus altering the shape of the MWD without requiring downstream blending.

Optimization results are summarized in Table I and shown in Figure 4. The hydrogen feed rate [Fig. 4(a)] starts oscillating, at time = 10 h, from its steady state value of 0.92 g/h. The characteristics of hydrogen pulses are summarized in Table I. The variations in hydrogen feed rate are high, which causes large fluctuations in hydrogen molar ratio,  $0.005 \leq X \leq 0.05$ , [Fig. 4(e)] inside the reactor. Even though the reactor is subjected to such severe oscillatory condi-

tions, the PDI of the resulting polymer differs very little ( $\sim 30\%$ ) from its steady state value. The figure shows also that there is a small increase in the number average molecular weight,  $M_{nc}$ , with respect to its steady state value [Fig. 4(f)]. This is attributed to the slight decrease in the effective molar ratio of hydrogen inside the reactor.

From Figure 4(d) it can be seen that controlling the polydispersity of the polymer has only a limited effect on the polymerization conversion,  $C$ . The reason for this behavior is that hydrogen molar ratio is high, it has therefore no effect on the polymerization rate; in



**Figure 4** Maximization of the polydispersity index with constant conversion through controlling  $F_{H_{2,in}}$ . (a)  $F_{H_{2,in}}$ , inlet hydrogen feed rate. (b)  $F_{cat,in}$ , inlet catalyst feed rate. (c) PDI, polydispersity index. (d)  $X$ , hydrogen to monomer molar ratio. (e)  $C$ , conversion. (f)  $T$ , reaction temperature. (g)  $M_{nc}$ , cumulative number average molecular weight.

addition, the catalyst concentration inside the reactor is constant. Such a result could be important in avoiding control system interactions in feedback control as well as allowing more flexibility in design.

So far, the resulted broadening is not high; thus, a different strategy will be investigated. This strategy is based on using both hydrogen and catalyst feed rates to control the broadening; subsequently, the conversion term will be omitted from the objective function, i.e.,  $w_2 = 0$ . The optimization leads to the results shown in Figure 5 and Table I. It is apparent from this figure that the maximum attainable PDI is increased to 9.97 ( $\sim 42\%$  increase in PDI). Note that the large fluctuations in catalyst feed rate lead to large fluctuations in monomer conversion as can be seen in Figure 5(f). This figure shows that the average conversion is low ( $\sim 0.1$ ); subsequently, this strategy is not economically visible and a different approach is required.

#### Maximum achievable broadening using forced hydrogen removal from the reactor

To achieve a higher polydispersity, while keeping the conversion high and PDI fluctuations low, a faster change in  $X$  should be made. Especially on the downward hydrogen step, the time between pulses might be reduced by faster decrease of  $X$ . One of the approaches to do so is using forced hydrogen removal.

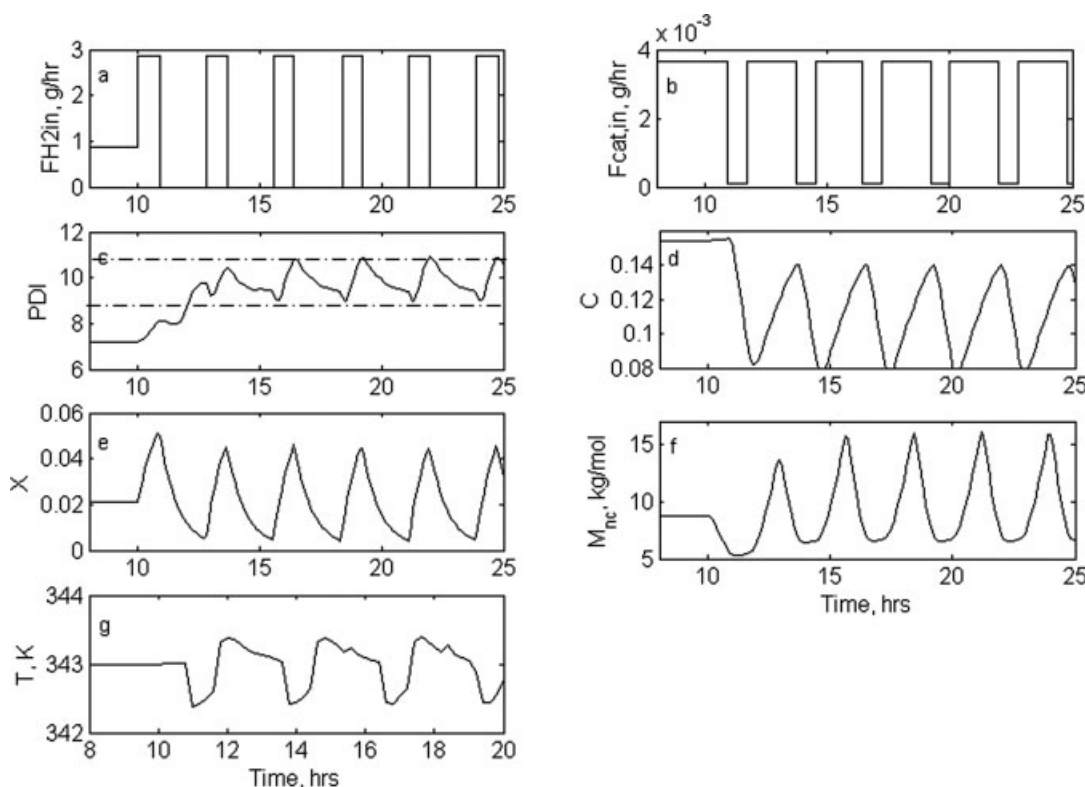
Until now, the decrease in hydrogen molar ratio takes place through washing the hydrogen out of the reactor. This decrease is gradual and requires a long time ( $\sim 2.5$  h) so that different polymer grades are produced within this transition period, which reduces the effect of the hydrogen pulses. If a forced hydrogen mechanism is considered, the change in hydrogen molar ratio becomes faster, which will lead to faster grade changes and therefore a higher PDI can be expected. This mechanism can take place in different ways. Discussing the suitable methods for hydrogen removal is beyond the scope of this study.

The increased level of hydrogen consumption is simulated by modifying the hydrogen component balance [eq. (A3)] into:

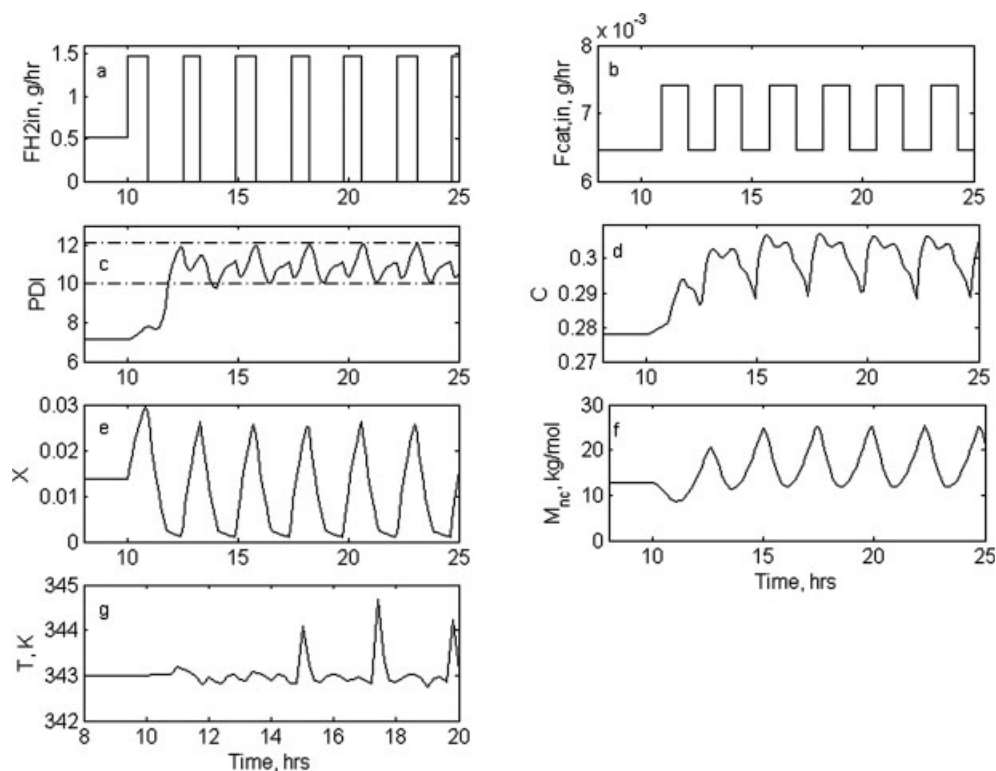
$$m \frac{dy_{H_2}}{dt} = F_{in}(y_{H_2,in} - y_{H_2}) - R_{H_2} - R_{removal} \quad (3)$$

where  $R_{removal}$  is the rate of forced hydrogen removal from the reactor in g/h. Note that to maximize the effect of such a term, it becomes "active" only when no hydrogen is added to the reactor. Figures 6 and 7 show the results for the maximum obtainable polydispersity; in case  $w_1 = 1$  and  $w_2 = 10$  (Fig. 6) and  $w_2 = 0$  (Fig. 7) and a forced hydrogen removal rate of 0.5 g/h.

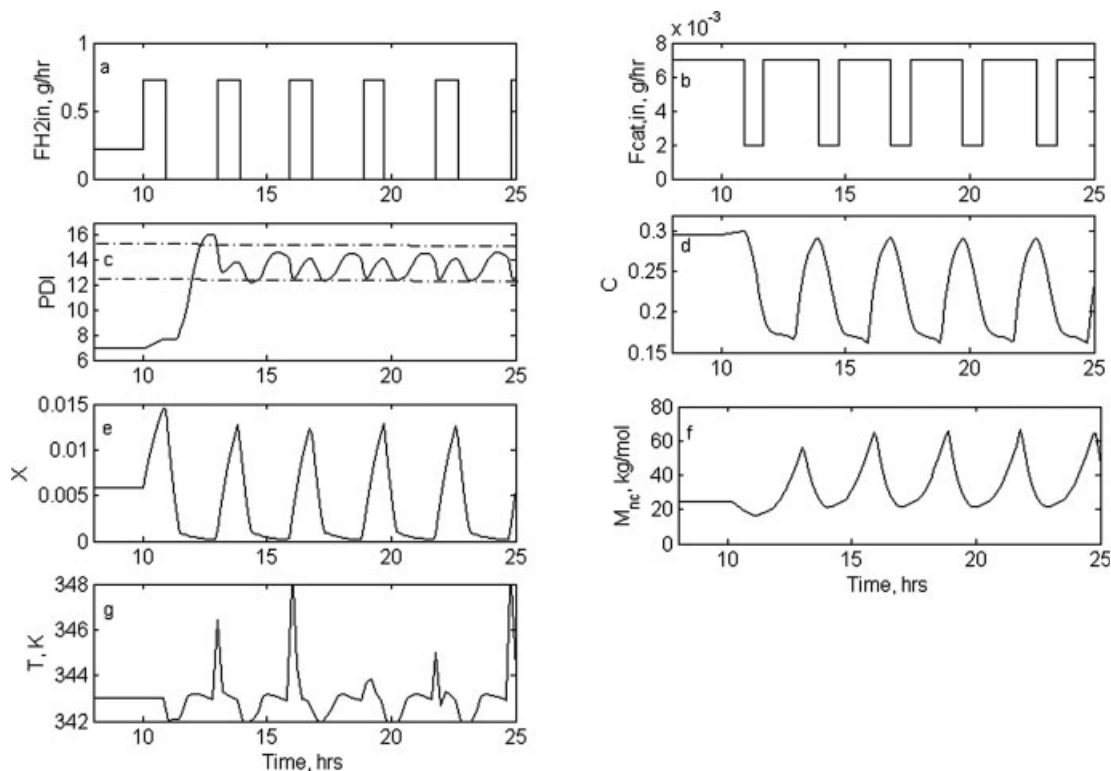
Figure 6 shows that the PDI can be increased to a value of 11.0, which is equivalent to a broadening



**Figure 5** Maximization of the polydispersity index with variable conversion through controlling  $F_{H_2,in}$  and  $F_{cat,in}$ .

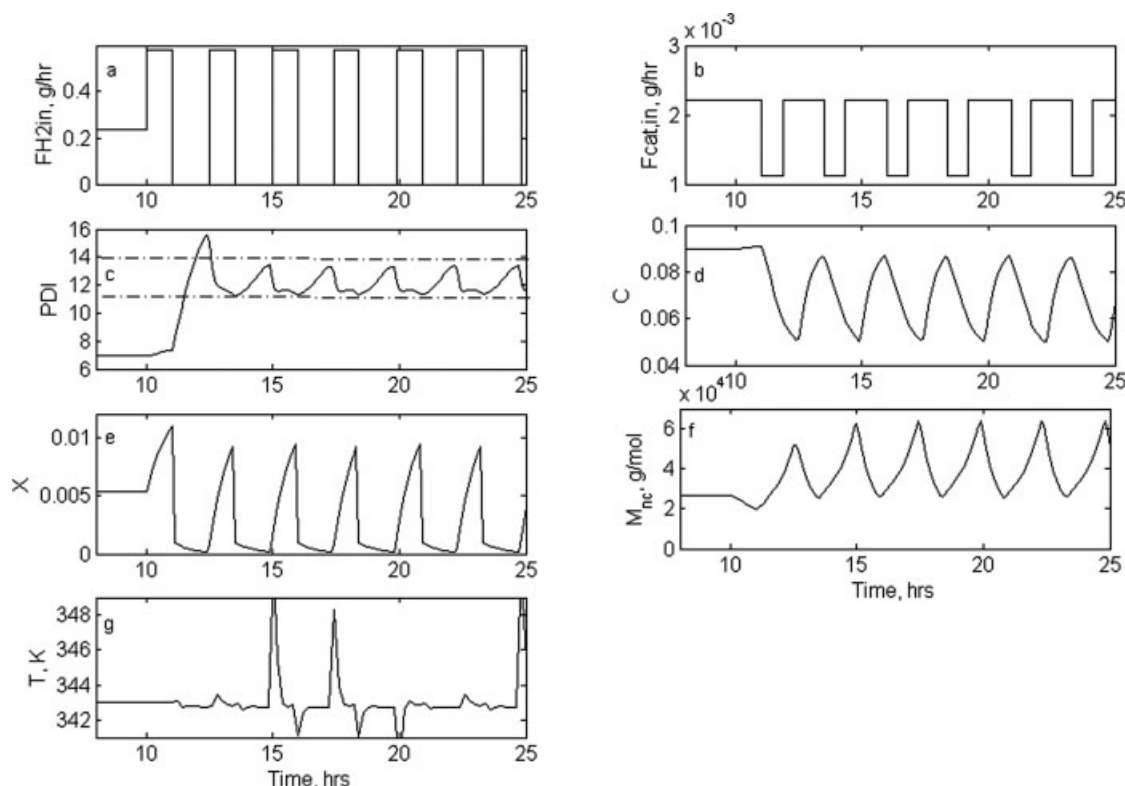


**Figure 6** Maximization of the polydispersity index with forced hydrogen removal of 0.5 g/h and small conversion fluctuations.



**Figure 7** Maximization of the polydispersity index with forced hydrogen removal of 0.5 g/h and large conversion fluctuations.





**Figure 8** Maximization of the polydispersity index with forced hydrogen removal of 50 g/h and large conversion fluctuations.

of 57%. This is achieved using a low hydrogen concentration inside the reactor ( $X_{\max} \sim 0.025$ ), which is half of the value used when hydrogen removal is not considered (Fig. 4). Note that large fluctuations in hydrogen molar ratio causes large changes in the polymerization rate, which is compensated by fluctuating catalyst feed rate; subsequently, the fluctuations in the reaction conversion become limited.

The MWD widening (nearly 100% in PDI) shown in Figure 7 indicates that the periodic operation of the polymerization reactor with forced hydrogen removal gives more flexibility to broaden the distribution compared with the steady state operation of the reactor.

The large changes in hydrogen molar ratio not only broaden the MWD but also shift it to higher chain length region. In case of forced hydrogen removal the mean hydrogen molar ratio is lower than that obtainable when hydrogen is washed out only. This leads to the production of polymers with a higher molecular weight, thus shifting the distribution towards higher chain lengths.

It is worth mentioning that a high hydrogen removal rate results either in low conversion or in high fluctuations in PDI but lower value of the PDI. To illustrate this, the results of the optimization using a hydrogen removal rate of 50 g/h are shown in Figure 8. For this case monomer conversion is not penalized. This figure shows that the obtained MWD

widening ( $\sim 75\%$ ), using a high hydrogen removal rate, is somewhat smaller than that obtained when lower hydrogen removal rate is used (Fig. 6). Moreover, the average conversion is around 7%, which is lower than that obtained using hydrogen removal rate of 0.5 g/h (average conversion  $\approx 20\%$ ). The reason for a low conversion is that the hydrogen concentration inside the reactor decreases fast at high hydrogen removal rate. This makes this case economically infeasible and an optimal hydrogen removal rate should be found for each practical situation.

It is worth mentioning that the overshoot in reaction temperature as shown in Figures 6–8, is because of the changing operating conditions in the reactor. To minimize this overshooting, the PI controller could be detuned.

#### Reactor residence time versus oscillation period

Reactor residence time is an important variable for practical purposes. For the studied system, the residence time is based on the inlet feed rate and it is time dependent due to the variation of the mass inside the reactor:

$$\tau(t) = \frac{m(t)}{F_{\text{in}}(t)} \quad (4)$$

Because of the relatively large changes in this variable during periodic operation, an average value,  $\bar{\tau}$ , will be used below. For the cases studied above,  $\bar{\tau}$  values are given in Table I.

The average residence time is compared with the corresponding optimal oscillation period,  $P$ , in terms of the ratio between the former and the latter,  $\frac{\bar{\tau}}{P}$  in Table I. The comparison shows that reactor residence time is approximately three times smaller than the period of oscillation. Note that this ratio is somewhat less,  $\sim 0.37$ , for two simulation runs. This is attributed to the fact that broadening can be considered as "mixing" of two distributions with specific fractions. In both cases, the reduction of hydrogen concentration inside the reactor is too fast to produce the required amounts of each fraction. Thus, hydrogen pulses are shorter than that for other cases.

In the simulations the values of  $P$  and  $\bar{\tau}$  are of the same order of magnitude, which can be expected. If this ratio is too large, this means that the cycle period is too large. In this case, the reactor will filter out the cycles; thus, its effect on the produced polymer will be limited. On the other hand, if the ratio is too small, the cycle period is high and it is not possible to have a broadened product.

Finally, notice that reactor residence time and cycle period are of the same order of magnitude. This means that the industrial application of this strategy requires cycle periods, which are of the same order of magnitude of the existing commercial processes,  $\sim 2\text{--}6$  h. This guarantees that the developed strategy is compatible with production schedules and may be implemented in practice.

## CONCLUSIONS

A feasibility study was performed to investigate whether the PDI of polypropylene could be increased using optimal periodic control of hydrogen and catalyst feed flows. To achieve this objective, a mathematical model was developed to describe the polymerization of liquid propylene in a continuous reactor. This model consisted of a set of balance equations and realistic kinetic and MWD models, which are developed using the results of kinetic experiments. Using control vector parameterization technique, the optimal cycle period and width for the manipulated inputs were determined. The following can be concluded:

1. The PDI can be increased by using a periodic hydrogen feed rate. However, broadening requires high-amplitude pulses and results in a limited widening ( $\sim 30\%$ ). This is obtained, while conversion variations are small.
2. Additional catalyst flow rate pulses can be used to decrease the fluctuations of PDI around its

average value; but this will lead to varying reaction conversion.

3. Using forced hydrogen removal from the reactor, a significantly higher PDI can be achieved without affecting the conversion or the need of high-amplitude hydrogen pulses. This results in broadening up to 100%. This might be at the expense of monomer conversion; thus, it is important to find an optimal hydrogen removal rate.
4. It is easier to broaden the MWD in batch reactors than in continuous polymerization reactors. This is attributed to the slow change in hydrogen concentration inside continuous reactors compared with batch reactors.
5. Possibilities for broadening the MWD depend strongly on the ability to remove hydrogen from the reactor. For example, the use of catalyst systems, which are highly sensitive to hydrogen, such as Ziegler-Natta catalyst with diether as an internal donor, might give better results than use of the existing catalyst. This is due to the fact that diether-catalyst is more sensitive to hydrogen, so that small amounts of hydrogen are required for polymer molecular weight control.

## NOTATION

$A$	Area of heat transfer ( $\text{m}^2$ )
$C$	Polymerization conversion
$C_{\text{sp}}$	Polymerization conversion set point
$C_{p,p}$	Polymer heat capacity ( $\text{kJ/kg K}$ )
$F$	Outlet flow rate from the reactor ( $\text{kg/h}$ )
$F_{\text{H}_2,\text{in}}$	Inlet hydrogen feed rate to the reactor ( $\text{g/h}$ )
$F_{\text{in}}$	Inlet flow rate to the reactor ( $\text{kg/h}$ )
$F_{\text{cat,in}}$	Inlet catalyst flow rate to the reactor ( $\text{g/h}$ )
$H$	Enthalpy of reactor contents ( $\text{MJ/kg}$ )
$H_{\text{in}}$	Enthalpy of the inlet material to the reactor ( $\text{MJ/kg}$ )
$j$	Number of repeating units in the produced polymer
$k_d$	Deactivation constant ( $1/\text{h}$ )
$k_p$	Propagation constant ( $\text{m}^3/\text{g}_{\text{cat}} \text{h}$ )
$k_1$	Temperature dependent variable
$k_2$	constant
$M$	Total mass inside the reactor ( $\text{kg}$ )
$m_i$	Mass fraction of polymer produced by active site, $i$
$m_p$	Polymer mass inside the reactor ( $\text{kg}$ )
$M_m$	Molecular weight of propylene monomer ( $\text{g/mol}$ )
$M_n$	Number average molecular weight ( $\text{g/mol}$ )
$M_w$	Weight average molecular weight ( $\text{g/mol}$ )

$P_n$	Number average molecular weight
PDI	Polydispersity index
$Q$	Termination probability
$R_{H_2}$	Hydrogen consumption rate (kg/h)
$R_p$	Polymerization rate (kg/h)
$R_{\text{removal}}$	Rate of forced hydrogen removal (g/h)
$T$	Polymerization temperature ( $^{\circ}\text{K}$ )
$t$	Time (h)
$U$	Heat transfer constant ( $\text{MJ/h m}^2 \text{ K}$ )
$V$	Reactor volume ( $\text{m}^3$ )
$w_i$	Weighing factor
$X$	Hydrogen molar ratio
$y_c$	Active catalyst mass fraction (g/kg)
$y_d$	Deactivated catalyst mass fraction (g/kg)
$y_{H_2}$	Hydrogen mass fraction (g/kg)
$y_j$	Cumulative molecular weight distribution
$y_m$	Monomer mass fraction (g/kg)
$y_j^d$	Instantaneous molecular weight distribution
$\rho$	Density of reactor contents ( $\text{kg/m}^3$ )
$\rho_m$	Monomer density ( $\text{kg/m}^3$ )
$\rho_p$	Polymer density ( $\text{kg/m}^3$ )

## APPENDIX A: MODEL EQUATIONS

The following assumptions were made to develop the model equations for the hollow shaft reactor:

1. At high mixing speeds ( $\geq 100$  rpm), the reactor content is ideally mixed. Thus, no temperature and concentration gradients are present and the growing polymer particles do not settle.<sup>30</sup>
2. The mass of the metal walls and its effects on the thermal dynamics are small and can be lumped with the reactor contents.
3. The reactor is always filled; no gas phase is present in the reactor.
4. The energy produced due to mixer rotation is negligible. This assumption is justifiable as long as the polymerization conversion, and as a result the viscosity of reactor content, does not change considerably during the polymerization reaction, which is the case.
5. A number of assumptions were made with respect to the polymerization mechanism and kinetics:
  1. Catalyst site activation is instantaneous.<sup>35</sup>
  2. Transfer reactions are assumed to form the same site type that is originally formed by activation of the catalyst by the cocatalyst.<sup>35</sup>
  3. The kinetic constants are independent of the chain length.<sup>36</sup>
  4. The catalyst decay through different chemical mechanisms at various types of active sites is lumped together into a single deactivation constant.<sup>37</sup> In addition, the active site concen-

tration decreases in accordance with a first order decay.<sup>38,39</sup>

6. Because of the high shear rates, the heat transfer through reactor wall is constant, i.e., no fouling occurs.<sup>30</sup>

In this investigation, it is assumed that the hollow shaft reactor contains two phases: (i) a liquid monomer phase and (ii) a polymer phase. The liquid phase consists of propylene monomer with dissolved hydrogen and the polymer phase consists of crystalline polymer and amorphous polymer, which is swollen with the monomer.

The overall mass balance of the reactor can be described as:

$$\frac{dm}{dt} = F_{\text{in}} - F \quad (\text{A1})$$

where  $m$  is the total mass inside reactor and  $F$  the outlet mass flow rate in kg/h,  $F_{\text{in}} = 1.0$  kg/h. The monomer mass balance is:

$$m \frac{dy_m}{dt} = F_{\text{in}} \cdot (y_{m,\text{in}} - y_m) - R_p \quad (\text{A2})$$

$y_m$  is the mass fraction of monomer in the outlet flow stream, and  $R_p$  is the propagation reaction rate. The hydrogen mass balance can be described as:

$$m \frac{dy_{H_2}}{dt} = F_{\text{in}}(y_{H_2,\text{in}} - y_{H_2}) - R_{H_2} \quad (\text{A3})$$

in which  $y_{H_2}$  is hydrogen mass fraction in  $\text{gH}_2/\text{kg}$  material inside the reactor,  $R_{H_2}$  is the hydrogen consumption rate. This "apparent" consumption rate is used since the reaction rate constants for transfer reactions with hydrogen and dormant sites reactivation are not known for the catalyst system used in this work. Assuming that all dead polymers are produced because of transfer through the hydrogen reaction, then the number of hydrogen moles consumed equals the number of polymer chains formed. The approximate number of these polymer chains is obtained using the number average degree of polymerization,  $P_n$ :

$$P_n = \frac{M_w}{\text{PDI}_{\text{avg}} M_m} \quad (\text{A4})$$

where  $\text{PDI}_{\text{avg}}$  is the average PDI. GPC measurements show that the average value of the PDI is approximately equal to 6.5.<sup>29</sup> The hydrogen consumption rate,  $R_{H_2}$ , can be calculated from:

$$R_{H_2} = \frac{2R_p}{M_m P_n} \quad (\text{A5})$$

where 2 is the molecular weight for a hydrogen molecule. Recalling the assumption that the catalyst is being activated before injecting it, the mass balance for the active catalyst,  $y_c$ , can be described as:

$$m \frac{dy_c}{dt} = F_{in} \cdot (y_{c,in} - y_c) - R_d \quad (A6)$$

in which  $R_d$  is the deactivation reaction rate. The concentration of the deactivated catalyst,  $y_d$ , can be calculated from the following balance:

$$m \frac{dy_d}{dt} = F_{in} \cdot (y_{d,in} - y_d) + R_d \quad (A7)$$

The reaction rates are calculated using the dormant site model<sup>31</sup>:

$$R_p = \frac{k_p m y_c \rho_m (1 + k_1 X)}{1 + k_2 + k_1 X} \quad (A8)$$

$$R_d = k_d m y_c \quad (A9)$$

where  $k_1$  is a temperature-dependent variable and  $k_2$  is a constant with a value of 8.02,  $k_p$  and  $k_d$  are rate constants,  $X$  is the molar ratio of hydrogen to propylene inside the reactor and  $\rho_m$  is the monomer density. Using the obtained monomer mole fraction, the monomer conversion is calculated from:

$$C = 1 - \frac{y_m}{y_{m,t=0}} \quad (A10)$$

The energy balance for the reactor can be written as:

$$m \frac{dH}{dt} = F_{in}(H_{in} - H) - R_p \Delta H_{R,p} - UA(T - T_{jacket}) \quad (A11)$$

The reactor energy balance takes into account the temperature-dependence of the monomer heat capacity; thus, the reactor temperature can be iteratively obtained from the following equation:

$$H = y_m \left[ a(T - T_{ref}) + \frac{b}{2}(T - T_{ref})^2 + \frac{c}{3}(T - T_{ref})^3 \right] + C_{p,p} y_p (T - T_{ref}) \quad (A12)$$

with  $T_{ref} = 273$  K,  $C_{p,p}$  is the heat capacity of the polymer that is assumed to have a constant value and  $a$ ,  $b$ , and  $c$  represent the coefficients of the polynomial that describes the monomer heat capacity. The values of these coefficients can be found in Al-haj Ali.<sup>29</sup>

Since the reactor is completely filled and there is a significant change in density because the low-density monomer is converted to the high-density polymer, the reactor outlet flow rate,  $F$ , will vary. It can be

shown that the following equation can be used to calculate this flow:

$$F = \left( \frac{F_{in}}{\rho_m} + R_p \left( \frac{1}{\rho_p} - \frac{1}{\rho_m} \right) - \left( \frac{dT}{dt} \right) m y_m \frac{\rho_{m,b} - 2\rho_{m,c}T}{\rho_m^2} \right) \rho \quad (A13)$$

where  $\rho_p$  is polymer density,  $\rho_m$  is the monomer density, which can be calculated from:

$$\rho_m = -\rho_{m,a} + \rho_{m,b}T - \rho_{m,c}T^2 \quad (A14)$$

$\rho$  is the density of the reaction mixture inside the reactor, it can be written as:

$$\rho = \frac{\rho_m \rho_p}{y_m \rho_p + y_p \rho_m} \quad (A15)$$

The instantaneous MWD,  $y_j^d$ , for olefin polymerization is given by Flory's most probable distribution:

$$y_j = j q^2 \exp(-j q) \quad (A16)$$

This equation is applicable to single-site catalysts. Thus, it is not possible to use this equation directly; instead the following equation should be used:

$$W = \sum_{i=1}^4 m_i y_{j,i}^d \quad (A17)$$

where  $W$  is the overall instantaneous MWD, and  $m_i$  is the mass fraction of each site.

The MWD of the polymer accumulated in the reactor after a certain polymerization time can be calculated using the following equation:

$$\frac{dy_j}{dt} = \frac{F_{in} \cdot (1 - y_{m,in})}{m_p} (y_{j,in} - y_j) + \frac{R_p}{m_p} (y_j^d - y_j) \quad (A18)$$

where  $y_j$  is the cumulative MWD and  $m_p$  is the mass of polymer accumulated inside the reactor.

It can be proved that the cumulative weight average molecular weight,  $M_w$ , can be calculated using the following equation:

$$\frac{dM_w}{dt} = \frac{R_p}{m_p} (M_w^d - M_w) \quad (A19)$$

where  $M_w^d$  is the instantaneous weight average molecular weight.

The relationship between the weight average molecular weight,  $M_w$ , and the termination probability,  $q$ , can be described as follows:

$$q = \frac{2M_m}{M_w} \quad (A20)$$



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